METHOD OF RECOVERING INORGANIC MATTER PARTS MATERIAL FROM ELECTRONIC PARTS USING SUPERCRITICAL WATER

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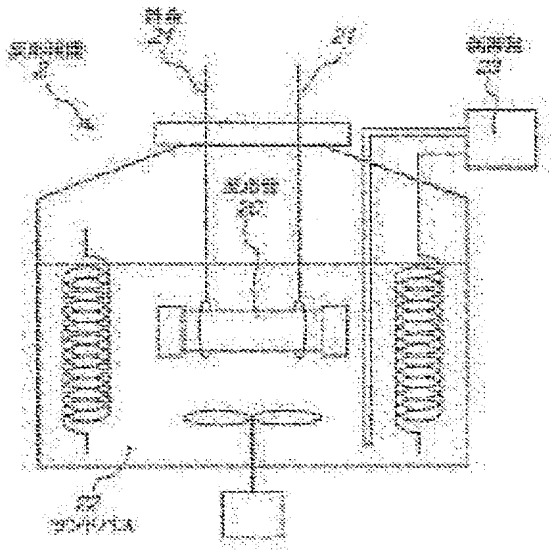
Abstract of **JP 2002233847 (A)**
PROBLEM TO BE SOLVED: To remove resin components of electronic parts composed of inorganic matter and the resin components by combining the oxidation decomposition by supercritical water and a swelling agent and to recover the inorganic matter in the state of an original form without entailing the change of the composition and the degradation in strength and function. SOLUTION: The electronic parts and the ultrapure water are put into a reaction tube 20 of a reaction apparatus 2 and both ends of the reaction tube are suspended by wires 21 and the reaction tube is immersed into a sand bath 22. The temperature and pressure in the reaction apparatus are controlled by a control panel 23 and the swelling by the addition of the swelling agent and the oxidation decomposition by the supercritical water are effected, by which the resin components are removed. The inorganic matter is recovered in a non-oxidizing state. The oxidation decomposition of the resin components by the supercritical water is preferably effected by setting the specific dielectric constant &epsi w of the supercritical water at 4<=&epsi w<=7 and ion product Kw at 14<=-LogKw<=17 and can be effected by adding an oxidizing agent thereto.



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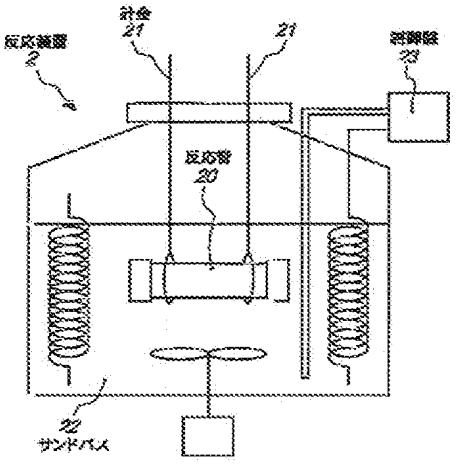
(54)【発明の名称】　超臨界水を用いた電子部品からの無機物部品材料の回収方法

(57)【要約】
【課題】無機物および樹脂成分から構成した電子部品において、超臨界水による酸化分解、および膨潤剤を組み合わせることで樹脂成分を除去するとともに、無機物については、組成の変化、強度や機能の低下等を伴わずに原形のまま回収して再使用する。
【解決手段】反応装置２内の反応管２０に、電子部品と超純水を入れ、反応管の両端を針金２１で懸垂してサンドバス２２に浸漬する。反応装置内の温度と圧力を制御盤２３により制御して、膨潤剤の添加による膨潤および超臨界水による酸化分解を行うことで樹脂成分を除去し、かつ、無機物については非酸化状態で回収する。超臨界水による樹脂成分の酸化分解においては、超臨界水の比誘電率εwを４≦εw≦７、イオン積Ｋwを１４≦－ＬｏｇＫw≦１７として行うことが好ましく、酸化剤を添加して行ってもよい。



【特許請求の範囲】
【請求項１】　所定形の部品材料が組み込まれて一定の機能を発揮する電子部品において、超臨界水により樹脂成分を酸化分解して除去するとともに、無機物については非酸化状態で回収することを特徴とする超臨界水を用いた電子部品からの無機物部品材料の回収方法。
【請求項２】　所定形の部品材料が組み込まれて一定の機能を発揮する電子部品において、膨潤剤の添加による膨潤および超臨界水による酸化分解を行うことで樹脂成分を除去し、かつ、無機物については非酸化状態で回収することを特徴とする超臨界水を用いた電子部品からの無機物部品材料の回収方法。
【請求項３】　樹脂成分の酸化分解を、
超臨界水の比誘電率ｅｗを４≦ｅｗ≦７、イオン積Ｋｗを１４≦－ＬｏｇＫｗ≦１７として行うことを特徴とする請求項１または２記載の超臨界水を用いた電子部品からの無機物部品材料の回収方法。
【請求項４】　超臨界水による樹脂成分の酸化分解を、樹脂成分の酸化剤を添加して行うことを特徴とする請求項１、２または３記載の超臨界水を用いた電子部品からの無機物部品材料の回収方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本願発明は、所定形の部品材料が組み込まれて一定の機能を発揮する電子部品からの無機物部品材料の回収方法に関し、特に、超臨界水の性質を利用して、電子部品の樹脂成分を酸化分解させて除去し、電子部品の基材などとして含有する珪素化合物や金属等の無機物については、組成の変化、強度や機能の低下等を伴わずに、無機物部品材料の部品性能を保ったまま回収することを目的とした方法に関する。
【０００２】
【従来の技術とその課題】近年、ＩＴ革命により電子部品は小型化、それに伴い部品材料はより小さく、より付加価値の高いものが増えてきている。しかし、小型化が進むにつれ製造工程が複雑になり製品の歩留率が悪く、ここで生じた機能不良の電子部品は廃棄物として、処分されているのが現状であった。
【０００３】これら不良品から有価無機物部品材料を回収する方法として、酸、アルカリや有機溶媒（例えばケトン類）で処理する方法がある。前者の処理法は、酸、アルカリによる部品材料の腐食や溶解が生じ、回収目的の物質の機能を毀損していた。　また、後者の処理法はケトン類（特にアセトン等）を用いるため、有機物は一度分解または溶解するが薄い膜となり無機物部品材料の表面を覆ってしまい、回収目的の無機物部品材料の性能を損ねる結果となっていた。
【０００４】このように、従来の処理方法では、電子部品の部品材料を原形のまま、すなわち、規格形状を損なうことなく、かつ物質の機能を毀損することなく回収することには問題があった。
【０００５】例えば、電子部品の例として水晶振動子について説明すると、水晶振動子は、水晶板とセラミック質のパッケージと、両者を接着する導電性の接着剤から構成されており、セラミックのパッケージ表面にはＷ、Ｎｉ－Ｃｏ、Ａｕ等が順に積層された端子が存在している。
【０００６】ところで、無機物質に影響を及ぼさず有機物質を分解する方法として、超臨界反応を用いた方法が近年着目されている。超臨界反応とは臨界温度・圧力以上で生じる反応である。例えば、水を反応媒体とした超臨界水は、無機物質はそのままに有機物質を水と二酸化炭素までに分解するものであるが、珪素化合物や金属等に代表される無機物質の組成の変化、強度や機能に影響を与えてしまうことがあり、実用化に至っていないのが現状である。
【０００７】
【目的】上記課題に鑑み、本願発明は、無機物および樹脂成分から構成した電子部品において、超臨界水による酸化分解、および必要に応じて添加される膨潤剤を組み合わせることで樹脂成分を除去するとともに、電子部品の基材などとして含有する無機物については、組成の変化、強度や機能の低下等を伴わずに原形のまま回収して再使用することを目的とした、新規な、超臨界水を用いた電子部品からの無機物部品材料の回収方法を提供するものである。
【０００８】
【課題を解決するための手段】上記目的を達成するため、本願発明にかかる超臨界水を用いた電子部品からの無機物部品材料の回収方法は以下のように構成している。
【０００９】すなわち、請求項１では、所定形の部品材料が組み込まれて一定の機能を発揮する電子部品を、超臨界水により樹脂成分を酸化分解して除去するとともに、無機物については非酸化状態で回収することを特徴とする。
【００１０】請求項２では、所定形の部品材料が組み込まれて一定の機能を発揮する電子部品において、膨潤剤の添加による膨潤および超臨界水による酸化分解を行うことで樹脂成分を除去し、かつ、無機物については非酸化状態で回収することを特徴とする。
【００１１】請求項３では、請求項１または２における樹脂成分の酸化分解を、超臨界水の比誘電率ｅｗを４≦ｅｗ≦７、イオン積Ｋｗを１４≦－ＬｏｇＫｗ≦１７として行うことを特徴とする。
【００１２】請求項４では、請求項１、２または３における樹脂成分の超臨界水による酸化分解を、樹脂成分の酸化剤を添加して行うことを特徴とする。
【００１３】超臨界水は、臨界温度（３７４．１℃）及び臨界圧力（２２．１ＭＰａ）を越えた領域の非凝縮性

の高密度水である。溶媒としての超臨界水は、温度或いは圧力を操作変数として、単一の溶媒でありながら複数の溶媒機能を有することが知られている。

【００１４】超臨界水の特性であるイオン積（Ｋｗ）については、常温常圧の水のイオン積がＫｗ＝１×１０↑（－１４）であるのに対して、温度および圧力の上昇とともに増大する。例えば、４００℃におけるイオン積は、臨界圧力以下の１０ＭＰａではＫｗ＝１×１０↑（－２８．５）であるのに対し、臨界圧力以上の３５ＭＰａではＫｗ＝１×１０↑（－１３．１）と大幅に増大する（－ＬｏｇＫｗは、２８．５から１３．１へと減少する）。すなわち、超臨界水には酸触媒やアルカリ触媒としての機能があることがわかる。

【００１５】超臨界水のもうひとつの特性である誘電率については、常温常圧の水の誘電率が７８程度であるのに対して、超臨界水では誘電率を温度と圧力の操作により２～３０程度の範囲で連続的且つ大幅に制御可能であることが挙げられる。例えば、４００℃における誘電率は、２５ＭＰａでは２．４であるが、５０ＭＰａでは１２となる。超臨界水の誘電率は、ヘキサン（誘電率は１．８程度）などの非極性溶媒から、メタノール（誘電率は３２．６）のような極性有機溶媒までの広範囲に相当する。従って、超臨界水を用いると、常温常圧の水には溶解しない有機物質を溶解することが可能となる。

【００１６】上述したような超臨界水の性質を、被回収無機物の組成に応じて利用することにより、無機物および樹脂成分から構成した電子部品の樹脂成分については酸化分解して除去することが可能となり、さらに、電子部品の基材などとして含有する珪素化合物や金属等の無機物については、組成の変化、強度や機能の低下等を伴わずに原形のまま回収して再使用することが可能となる。

【００１７】本願発明を実施するための温度および圧力は、水の臨界温度および臨界圧力の近傍やそれ以上の範囲であれば特に限定はされない。しかしながら、超臨界水の比誘電率ｅｗが４≦ｅｗ≦７、イオン積Ｋｗが１４≦－ＬｏｇＫｗ≦１７であれば速やかに樹脂成分の分解反応を進行させ、かつ、無機物については、組成の変化、強度や機能の低下等を伴わずに回収することが可能となる。本願発明の超臨界水を用いた電子部品からの無機物部品材料の回収方法の環境としては、反応装置や操作の問題などを考慮すると、３８０～４３０℃、２４～３５ＭＰａで上記反応条件を実現可能であり、必ずしもこれ以上に高くする必要はない。

【００１８】本願発明の実施対象となる電子部品における回収対象の無機物は、組成の変化、強度や機能の低下等を伴わずに回収できれば、形状や物質種を限定するものではない。アルミナ、酸化チタン、酸化珪素などの酸化物、窒化アルミニウムなどの窒化物、炭酸カルシウム、タルク、石英、ガラス、ケイ砂や金属などの天然物を含む無機物や金属箔が例として挙げられる。

【００１９】また、本願発明の実施対象となる電子部品における樹脂成分は、熱硬化性あるいは熱可塑性のいずれの樹脂でもよく、２種類以上の成分からなるポリマーアロイやそれらの混合物、あるいは積層物でもよい。さらに、従来は分解が難しかったエポキシ樹脂やフェノール樹脂の硬化物も対象にすることができる。

【００２０】加えて、超臨界水を用いた本願発明の実施における樹脂成分用の膨潤剤等としては、カルボン酸類、アルコール類、ケトン類、窒素、二酸化炭素等からなる群より選ばれた1種類以上を、超臨界水による反応前、反応中、反応後に添加するようにしてもよい。樹脂成分の膨潤と超臨界水による酸化反応が同時、或いはいずれか一方が先に進行した場合であっても、これらの相加的、相乗的あるいは補完的作用のいずれかまたは組み合わせにより樹脂成分の除去に寄与するからである。上記カルボン酸類としては酢酸、乳酸等が好ましく、アルコール類ではメチルアルコール、エチルアルコール等が好ましく、酸化剤としては、過酸化水素、酸素、空気、オゾン等の酸素供給物質が好ましい。

【００２１】なお、本願発明で使用する樹脂成分が、ハロゲン、硫黄やリン化合物等を含有する場合、塩基性物質である水酸化ナトリウムなどの中和剤を、添加剤として混合することにより、ハロゲン化ナトリウム、硫酸ナトリウム、リン酸ナトリウム等の塩として中和するようにしてもよい。

【００２２】

【発明の実施の形態】以下に本願発明にかかる超臨界水を用いた電子部品からの無機物部品材料の回収方法について詳細に説明する。図１は本実施形態の電子部品からの無機物部品材料の回収方法に用いた水晶振動子の説明図であり、図２は本実施形態の電子部品からの無機物部品材料の回収方法に用いた反応装置の説明図である。

【００２３】本実施形態における電子部品としては、生産工場で発生した機能不良のＭＳＤ（表面実装）水晶振動子１（以下、「水晶振動子１」と省略。）を用いた。水晶振動子１は、水晶板１０と金属配線付のセラミック質のパッケージ１１からなる無機物と、水晶板１０とパッケージ１１を接着する導電性接着剤１２からなる有機物から構成されている。このセラミックのパッケージ１１表面にはＷ、Ｎｉ－Ｃｏ、Ａｕ等が順に積層された端子１１ａが存在している。

【００２４】反応装置２内の反応管２０（容積は６ｍＬ）に、水晶振動子１と超純水を約３．０ｇ入れ（実施例によっては添加剤を加えた。）、反応管２０の両端を針金２１で懸垂してサンドバス２２に浸漬して、反応装置２内の温度と圧力を制御盤２３により制御して実験を行った。以下の実施例、比較例では、サンドバス２２に投入した時点で反応開始とし、所定時間経過後にサンドバス２２より反応管２０を取り出して急冷し、超臨界水

処理後、有機物脱脂工程および水洗工程を経て乾燥したものに対して特性評価を行った。

【００２５】

【実施例１】実施例１は、水晶振動子１を膨潤剤に浸漬させてから、臨界温度・圧力以上の水を用い超臨界反応を行った。実施条件は、温度；４００℃、圧力；２８．９ＭＰａで超臨界反応を行った。膨潤剤は、乳酸１０ｍＬに対し、エタノールを１００ｍＬの割合で調合し、その０．０５ｇを超純水３ｇに加えた。

【００２６】以上の条件で実施したところ、反応時間は１０ｍｉｎで水晶板１０とセラミックパッケージ１１を接着している導電性接着剤１２を分解することができた。それにより、有価無機物部品材料である水晶板１０とセラミックパッケージ１１を回収することができた。

【００２７】実施例１で回収した水晶板１０とセラミックパッケージ１１の機能特性を測定した。表１は回収した水晶板１０とセラミックパッケージ１１の諸特性を測定した表であり、水晶板１０の周波数は新品の部品材料と同特性を得ることができた。また、セラミックパッケージ１１の端子１１ａの膜厚と絶縁抵抗値も新品の部品材料と同特性を得ることができた。

【００２８】実施例１により、超臨界反応の前に電子部品を膨潤剤に浸漬させ、超臨界水反応を行うことにより短時間で無機物部品材料を回収し再使用する方法を提供することができた。

【００２９】

【実施例２】実施例２は、水晶振動子１を膨潤剤に浸漬させてから、臨界温度・圧力以上の水を用い超臨界反応を行った。実施条件は、温度；３８０℃、圧力；２４．３ＭＰａで超臨界反応を行った。膨潤剤の混合については実施例１と同様とした。

【００３０】以上の条件で実施したところ、反応時間は３０ｍｉｎで水晶板１０とセラミックパッケージ１１を接着している導電性接着剤１２を分解することができた。それにより、有価無機物部品材料である水晶板１０とセラミックパッケージ１１を回収することができた。

【００３１】実施例２で回収した水晶板１０とセラミックパッケージ１１の機能特性を測定した。表１により、水晶板１０の周波数は新品の部品材料と同特性を得ることができた。また、セラミックパッケージ１１の端子１１ａの膜厚と絶縁抵抗値も新品の部品材料と同特性を得ることができた。

【００３２】実施例２により、超臨界反応の前に電子部品を膨潤剤に浸漬させ、超臨界水反応を行うことにより短時間で有価無機物部品材料を回収しリサイクルする方法を提供することができた。

【００３３】

【実施例３】実施例３は、水晶振動子１を臨界温度・圧力以上の添加剤の入った水を用い超臨界反応を行った。実施条件は、温度；４００℃、圧力；２８．９ＭＰａで超臨界反応を行った。膨潤剤の混合については実施例１と同様とした。

【００３４】以上の条件で実施したところ、反応時間は３０ｍｉｎで水晶板１０とセラミックパッケージ１１を接着している導電性接着剤１２を分解することができた。それにより、有価無機物部品材料である水晶板１０とセラミックパッケージ１１を回収することができた。

【００３５】実施例３で回収した水晶板１０とセラミックパッケージ１１の機能特性を測定した。表１により水晶板１０の周波数は新品の部品材料と同特性を得ることができた。また、セラミックパッケージ１１の端子１１ａの膜厚と絶縁抵抗値も新品の部品材料と同特性を得ることができた。

【００３６】実施例３により、水に添加剤を少量加え超臨界反応を行うことにより短時間で有価無機物部品材料を回収しリサイクルする方法を提供することができた。

【００３７】

【実施例４】実施例４は、水晶振動子１を臨界温度・圧力以上の添加剤の入った水を用い超臨界反応を行った。実施条件は、温度；３８０℃、圧力；２４．３ＭＰａで超臨界反応を行った。膨潤剤の混合については実施例１と同様とした。

【００３８】以上の条件で実施したところ、反応時間は６０ｍｉｎで水晶板１０とセラミックパッケージ１１を接着している導電性接着剤１２を分解することができた。それにより、有価無機物部品材料である水晶板１０とセラミックパッケージ１１を回収することができた。

【００３９】実施例４で回収した水晶板１０とセラミックパッケージ１１の機能特性を測定した。表１により、水晶板１０の周波数は新品の部品材料と同特性を得ることができた。また、セラミックパッケージ１１の端子１１ａの膜厚と絶縁抵抗値も新品の部品材料と同特性を得ることができた。

【００４０】実施例４により、水に添加剤を少量加え超臨界反応を行うことにより有価無機物部品材料を回収しリサイクルする方法を提供することができた。

【００４１】

【実施例５】実施例５として、膨潤剤を用いずに水晶振動子１を臨界温度・圧力以上の水で超臨界反応を行った。比較条件は、温度；４００℃、圧力；２８．９ＭＰａで超臨界反応を行った。

【００４２】以上の条件で比較したところ、反応時間は６０ｍｉｎで水晶板１０とセラミックパッケージ１１を接着している導電性接着剤１２を分解することができた。それにより、有価無機物部品材料である水晶板１０とセラミックパッケージ１１を回収することができた。しかし、実施例１～３で行った以上の反応時間が必要になった。

【００４３】次に、実施例５で回収した水晶板１０とセラミックパッケージ１１の機能特性を測定した。表１に

より、水晶板１０の周波数は新品の部品材料と同特性であった。また、セラミックパッケージ１１の端子１１ａの膜厚と絶縁抵抗値も新品の部品材料と同特性であった。

【００４４】

【比較例１】水晶振動子１を膨潤剤に浸漬させてから、臨界温度・圧力以下の水を用い亜臨界反応を行った。比較条件は、温度：２８０℃、圧力：８．２ＭＰａで亜臨界反応を行った。膨潤剤の混合については実施例１と同様とした。

【００４５】以上の条件で比較したところ，亜臨界反応を１８０分間行ったところ、水晶板１０とセラミックパッケージ１１を接着している導電性接着剤１２は分解することができなかった。また、有価無機物部品材料である水晶板１０は亜臨界反応の影響により、粉々に破壊されていたため評価を行うことができなかった。

【００４６】

【表１】

	温度 (℃)	圧力 (MPa)	膨潤剤	時間 (min.)	水晶板 周波数 (MHz)	セラミックパッケージ 端子膜厚 (μm)	セラミックパッケージ 絶縁抵抗 ($\times 10^8\Omega$)
実施例1	400	28.8	あり	10	14.4	1.45	2.47
実施例2	380	24.3	あり	30	14.4	1.43	2.35
実施例3	400	28.8	あり	30	14.4	1.45	2.49
実施例4	380	24.3	あり	60	14.4	1.44	2.43
実施例5	400	28.9	なし	60	14.4	1.45	2.49
比較例1	280	8.2	あり	180	破壊	破壊	破壊
規格値	-	-	-	-	14.3-14.5	1.0-3.0	$<2.0\times10^8$

【００４７】

【発明の効果】以上の実施例からもわかるように、本願発明によれば機能不良で生じた電子部品を，必要に応じて膨潤剤や酸化剤を加えた水に浸漬させ、臨界温度・圧力以上の超臨界水を用いることで，樹脂成分の膨潤と超臨界水による酸化反応を相加的、相乗的あるいは補完的作用のいずれかまたは組み合わせにより行って樹脂成分を除去し、有価無機物部品材料については組成の変化、強度や機能の低下等を伴わずに回収して再利用することができる。

【００４８】また、本願発明の実施対象となる樹脂成分は、熱硬化性あるいは熱可塑性のいずれの樹脂でもよく、２種類以上の成分からなるポリマーアロイやそれらの混合物、あるいは積層物、さらに、従来は分解が難しかったエポキシ樹脂やフェノール樹脂の硬化物も対象にすることができ、酸やアルカリを大量に使用しないため大掛かりな中和設備を必要とせずコスト的に有利になるなど、その産業的効果は顕著なものである。

【図面の簡単な説明】

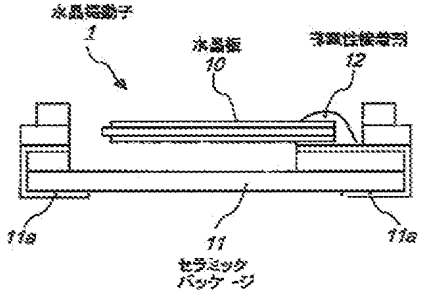
【図１】　本実施形態の電子部品からの無機物部品材料の回収方法に用いた水晶振動子の説明図である。

【図２】　本実施形態の電子部品からの無機物部品材料の回収方法に用いた反応装置の説明図である。

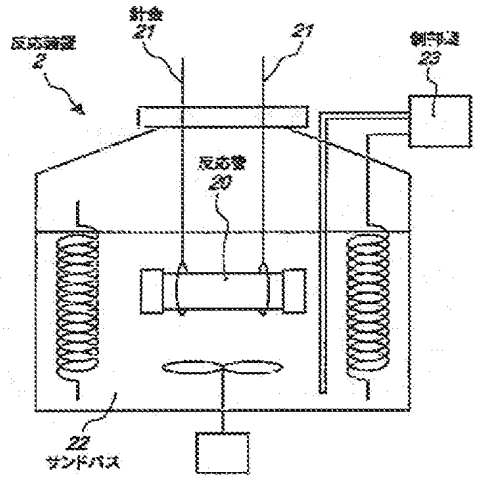
【符号の説明】

１　水晶振動子
１０　水晶板
１１　セラミックパッケージ
１１ａ　端子
１２　導電性接着剤
２　反応装置
２０　反応管
２１　針金
２２　サンドバス
２３　制御盤

【図１】



【図2】



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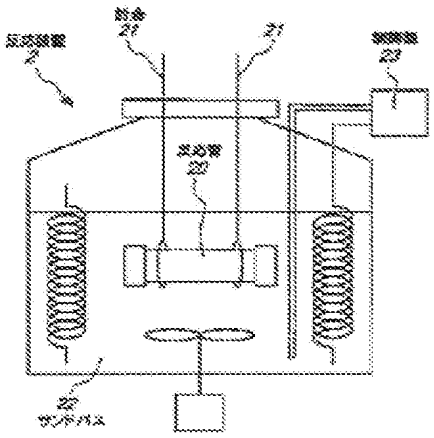
(54) METHOD OF RECOVERING INORGANIC MATTER PARTS MATERIAL FROM ELECTRONIC PARTS USING SUPERCRITICAL WATER

(57)Abstract:
PROBLEM TO BE SOLVED: To remove resin components of electronic parts composed of inorganic matter and the resin components by combining the oxidation decomposition by supercritical water and a swelling agent and to recover the inorganic matter in the state of an original form without entailing the change of the composition and the degradation in strength and function.
SOLUTION: The electronic parts and the ultrapure water are put into a reaction tube 20 of a reaction apparatus 2 and both ends of the reaction tube are suspended by wires 21 and the reaction tube is immersed into a sand bath 22. The temperature and pressure in the reaction apparatus are controlled by a control panel 23 and the swelling by the addition of the swelling agent and the oxidation decomposition by the supercritical water are effected, by which the resin components are removed. The inorganic matter is recovered in a non-oxidizing state. The oxidation decomposition of the resin components by the supercritical water is preferably effected by setting the specific dielectric constant εw of the supercritical water at 4≤εw≤7 and ion product Kw at 14≤-LogKw≤17 and can be effected by adding an oxidizing agent thereto.



* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]A recovery method of an inorganic substance part material from electronic parts using supercritical water characterized by collecting by a non-oxidation state about an inorganic substance while carrying out oxidative degradation of the resinous principle with supercritical water and removing in electronic parts which a part material of a predetermined shape is incorporated and exhibit a fixed function.
[Claim 2]In electronic parts which a part material of a predetermined shape is incorporated and exhibit a fixed function, A recovery method of an inorganic substance part material from electronic parts using supercritical water removing a resinous principle by performing swelling by addition of a swelling agent, and oxidative degradation by supercritical water, and collecting by a non-oxidation state about an inorganic substance.
[Claim 3]A recovery method of an inorganic substance part material from electronic parts using the supercritical water according to claim 1 or 2 performing [oxidative degradation of a resinous principle] 4<=epsilonw<=7 and the ionic product Kw for specific-inductive-capacity epsilonw of supercritical water as 14 <=-LogKw<=17.
[Claim 4]A recovery method of an inorganic substance part material from electronic parts using the supercritical water according to claim 1, 2, or 3 adding an oxidizer of a resinous principle and performing oxidative degradation of a resinous principle by supercritical water.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]The invention in this application uses the character of supercritical water especially about the recovery method of the inorganic substance part material from the electronic parts which the part material of a predetermined shape is incorporated and exhibit a fixed function. Oxidative degradation of the resinous principle of electronic parts is carried out, and it removes, and is related with the method aiming at collecting with the part performance of an inorganic substance part material maintained without being accompanied by change of a presentation, intensity, the fall of a function, etc. about inorganic substances contained as a substrate of electronic parts, etc., such as a silicon compound and metal.
[0002]
[Description of the Prior Art]In recent years, in connection with a miniaturization and it, what [electronic parts'] has added value smaller a part material and higher is increasing by IT revolution. However, the manufacturing process became complicated, the yield rate of the product was bad and the actual condition was that the electronic parts of malfunctioning produced here are disposed of as waste as the miniaturization progressed.
[0003]Methods of collecting valuable inorganic substance part materials from these inferior goods include the method of processing with acid, alkali, or an organic solvent (for example, ketone). The corrosion and the dissolution of a part material by acid and alkali arose, and the former approach had damaged the function of the substance for the purpose of recovery. In order that the latter approach might use ketone (especially acetone etc.), although it decomposed or dissolved once, the organic matter became a thin film, covered the surface of the inorganic substance part material, and had resulted in spoiling the performance of the inorganic substance part material for the purpose of recovery.
[0004]Thus, in the conventional disposal method, there was a problem in collecting without [without it spoils the part material of electronic parts with the original form (i.e., standard shape), and] damaging the function of a substance.
[0005]For example, if a crystal oscillator is explained as an example of electronic parts, the crystal oscillator comprises conductive adhesives on which a quartz plate and the quality of ceramics pack and both are pasted up.
The terminal in which W, nickel-Co, Au, etc. were laminated in order exists in the package surface of ceramics.

[0006]By the way, its attention is paid to the method using the supercritical reaction as a method which does not affect mineral matter but disassembles an organic substance in recent years. A supercritical reaction is a reaction produced above critical temperature and a pressure. For example, the actual condition is that the supercritical water which used water as the reaction medium may affect change, and the intensity and the function of mineral matter of a presentation which are represented by a silicon compound, metal, etc., and has not resulted in utilization although mineral matter disassembles an organic substance even into water and carbon dioxide as it is.
[0007]
[Objects of the Invention]While removing a resinous principle because the invention in this application combines the oxidative degradation by supercritical water, and the swelling agent added if needed in

view of an aforementioned problem in the electronic parts constituted from an inorganic substance and a resinous principle. About the inorganic substance contained as a substrate of electronic parts, etc., the recovery method of the inorganic substance part material from the electronic parts using new supercritical water aiming at collecting with the original form and carrying out a reuse, without being accompanied by change of a presentation, intensity, the fall of a function, etc., is provided.
[0008]
[Means for Solving the Problem]In order to attain the above-mentioned purpose, a recovery method of an inorganic substance part material from electronic parts using supercritical water concerning the invention in this application is constituted as follows.
[0009]That is, at Claim 1, while carrying out oxidative degradation of the resinous principle with supercritical water and removing electronic parts which a part material of a predetermined shape is incorporated and exhibit a fixed function, about an inorganic substance, it collects by a non-oxidation state.
[0010]In Claim 2, in electronic parts which a part material of a predetermined shape is incorporated and exhibit a fixed function, a resinous principle is removed by performing swelling by addition of a swelling agent, and oxidative degradation by supercritical water, and a non-oxidation state recovers an inorganic substance.
[0011]In Claim 3, 4<=epsilonw<=7 and the ionic product Kw are performed [oxidative degradation of Claim 1 or a resinous principle in 2] for specific-inductive-capacity epsilonw of supercritical water as 14 <=-LogKw<=17.
[0012]In Claim 4, an oxidizer of a resinous principle is added and Claim 1 and oxidative degradation by supercritical water of a resinous principle in 2 or 3 are performed.
[0013]Supercritical water is non-condensable high-density water of a field beyond critical temperature (374.1 **) and the critical pressure (22.1MPa). Supercritical water as a solvent makes temperature or a pressure an instrumental variable, and though it is a single solvent, having two or more solvent functions is known.
[0014]About an ionic product (Kw) which is the characteristic of supercritical water, it increases with a rise of temperature and a pressure to an ionic product of water of ordinary temperature ordinary pressure being Kw=1x10** (-14). For example, an ionic product at 400 ** increases substantially with Kw=1x10** (-13.1) by 35MPa more than the critical pressure to being Kw=1x10** (-28.5) in 10MPa below the critical pressure (-LogKw decreases from 28.5 to 13.1). That is, it turns out that supercritical water has a function as an acid catalyst or an alkali catalyst.
[0015]About a dielectric constant which is another characteristic of supercritical water, a thing controllable continuously and substantially is mentioned by operation of temperature and a pressure in the about two to 30 range in a dielectric constant with supercritical water to a dielectric constant of water of ordinary temperature ordinary pressure being about 78. For example, although a dielectric constant at 400 ** is 2.4 in 25MPa, it is set to 12 by 50MPa. A dielectric constant of supercritical water is equivalent to a large area from nonpolar solvents, such as hexane (a dielectric constant is about 1.8), to a polar organic solvent like methanol (a dielectric constant is 32.6). Therefore, if supercritical water is used, it will become possible to dissolve an insoluble organic substance in water of ordinary temperature ordinary pressure.
[0016]By using character of supercritical water which was mentioned above according to a presentation of an inorganic substance to be collected, it becomes possible to carry out oxidative degradation and to remove about a resinous principle of electronic parts constituted from an inorganic substance and a resinous principle. About inorganic substances contained as a substrate of electronic parts, etc., such as a silicon compound and metal, it becomes possible to collect with the original form and to carry out a reuse, without being accompanied by change of a presentation, intensity, a fall of a function, etc.
[0017]If a range near critical temperature of water and the critical pressure of temperature and a pressure for carrying out the invention in this application is beyond it, limitation in particular will not be carried out. However, it becomes possible to collect without advancing a decomposition reaction of a resinous principle promptly, if specific-inductive-capacity epsilonw of supercritical water is 4<=epsilonw<=7 and the ionic product Kw is 14 <=-LogKw<=17, and being accompanied by change of a presentation, intensity, a fall of a function, etc. about an inorganic substance. As environment of a recovery method of an inorganic substance part material from electronic parts using supercritical

water of the invention in this application, if a reaction apparatus, a problem of operation, etc. are taken into consideration, the above-mentioned reaction condition can be realized and it is not necessary to necessarily make it higher than this by 350-430 ** and 24 - 35MPa.
[0018]An inorganic substance for [in electronic parts which are the operation targets of the invention in this application] recovery will limit neither shape nor a substance kind, if it can collect without being accompanied by change of a presentation, intensity, a fall of a function, etc. An inorganic substance and a metallic foil including a natural product of nitrides, such as oxides, such as alumina, titanium oxide, and oxidized silicon, and aluminium nitride, calcium carbonate, talc, quartz, glass, silica, metal, etc. are mentioned as an example.
[0019]Which thermosetting or thermoplastic resin may be sufficient as a resinous principle in electronic parts which are the operation targets of the invention in this application, and polymer alloys which consist of two or more kinds of ingredients, those mixtures, or laminated material may be sufficient as it. A hardened material of an epoxy resin for which decomposition was difficult, or phenol resin can also be conventionally made into an object.
[0020]In addition, it may be made to add one or more kinds chosen from a group which consists of carboxylic acid, alcohols, ketone, nitrogen, carbon dioxide, etc. as a swelling agent for resinous principles in operation of the invention in this application using supercritical water, etc. before a reaction by supercritical water, during a reaction, and after a reaction. Even if it is a case where simultaneous [oxidation reaction by swelling and supercritical water of a resinous principle] or either advances previously, it is because it contributes to removal of a resinous principle with either or combination of these additive, synergistic, or complementary operations. As the above-mentioned carboxylic acid, acetic acid, lactic acid, etc. are preferred, in alcohols, methyl alcohol, ethyl alcohol, etc. are preferred and oxygen supply substances, such as hydrogen peroxide, oxygen, air, and ozone, are preferred as an oxidizer.
[0021]By mixing neutralizers, such as sodium hydroxide which is an alkali, as an additive agent, when a resinous principle used by the invention in this application contains halogen, sulfur, phosphorus compounds, etc., It may be made to neutralize as salts, such as sodium halide, sodium sulfate, and sodium phosphate.
[0022]
[Embodiment of the Invention]The recovery method of the inorganic substance part material from the electronic parts using the supercritical water concerning the invention in this application is explained in detail below. Drawing 1 is an explanatory view of the crystal oscillator used for the recovery method of the inorganic substance part material from the electronic parts of this embodiment, and drawing 2 is an explanatory view of the reaction apparatus used for the recovery method of the inorganic substance part material from the electronic parts of this embodiment.
[0023]As electronic parts in this embodiment, the MSD (surface mount) crystal oscillator 1 (it abbreviates to "the crystal oscillator 1" hereafter.) of malfunctioning by which it was generated at the production plant was used. The crystal oscillator 1 comprises an inorganic substance which consists of the package 11 of the quality of ceramics the quartz plate 10 and with metallic wiring, and an organic matter which consists of the electroconductive glue 12 on which the quartz plate 10 and the package 11 are pasted up. The terminal 11a in which W, nickel-Co, Au, etc. were laminated in order exists in the package 11 surface of these ceramics.
[0024]It experimented on the coil 20 (capacity is 6mL) in the reaction apparatus 2 by putting in the crystal oscillator 1 and about 3.0g of ultrapure water (the additive agent was added depending on working example.), hanging with the wire 21, immersing the both ends of the coil 20 in the sand bath 22, and controlling the temperature and the pressure in the reaction apparatus 2 by the operator control panel 23. In the following working example and a comparative example, when supplied to the sand bath 22, it was considered as the reaction start, and the coil 20 was taken out and quenched from the sand bath 22 after specified time elapse, and characterization was performed after supercritical water treatment to the thing dry through the organic matter degreasing process and the washing process.
[0025]
[Work example 1]Working example 1 performed the supercritical reaction using the water more than critical temperature and a pressure, after making the crystal oscillator 1 immersed in a swelling agent. The operation condition performed the supercritical reaction by temperature;400 ** and

pressure;28.9MPa. To lactic acid 10mL, the swelling agent prepared ethanol at a rate of 100mL, and added the 0.05 g to the ultrapure water 3g.
[0026]When carried out on condition of above, the reaction time was able to disassemble the electroconductive glue 12 on which the quartz plate 10 and the ceramic package 11 are pasted up by 10min. Thereby, the quartz plates 10 and the ceramic packages 11 which are valuable inorganic substance part materials were able to be collected.
[0027]The functional characteristic of the quartz plate 10 collected in working example 1 and the ceramic package 11 was measured. Table 1 is the collected quartz plate 10 and a table which measured the various characteristics of the ceramic package 11, and the frequency of the quartz plate 10 was able to obtain a new part material and the characteristic. The thickness and the insulation resistance value of the terminal 11a of the ceramic package 11 were also able to obtain a new part material and the characteristic.
[0028]According to working example 1, the swelling agent was able to be made to have been able to immerse electronic parts before a supercritical reaction, and the method of collecting and carrying out the reuse of the inorganic substance part material for a short time was able to be provided by performing a supercritical water reaction.
[0029]
[Work example 2]Working example 2 performed the supercritical reaction using the water more than critical temperature and a pressure, after making the crystal oscillator 1 immersed in a swelling agent. The operation condition performed the supercritical reaction by temperature;380 ** and pressure;24.3MPa. About mixing of the swelling agent, it was presupposed that it is the same as that of working example 1.
[0030]When carried out on condition of above, the reaction time was able to disassemble the electroconductive glue 12 on which the quartz plate 10 and the ceramic package 11 are pasted up by 30min. Thereby, the quartz plates 10 and the ceramic packages 11 which are valuable inorganic substance part materials were able to be collected.
[0031]The functional characteristic of the quartz plate 10 collected in working example 2 and the ceramic package 11 was measured. By Table 1, the frequency of the quartz plate 10 was able to obtain a new part material and the characteristic. The thickness and the insulation resistance value of the terminal 11a of the ceramic package 11 were also able to obtain a new part material and the characteristic.
[0032]According to working example 2, the swelling agent was able to be made to have been able to immerse electronic parts before a supercritical reaction, and the method of collecting and recycling a valuable inorganic substance part material for a short time was able to be provided by performing a supercritical water reaction.
[0033]
[Work example 3]Working example 3 performed the supercritical reaction using the water into which the additive agent more than critical temperature and a pressure went the crystal oscillator 1. The operation condition performed the supercritical reaction by temperature;400 ** and pressure;28.9MPa. About mixing of the swelling agent, it was presupposed that it is the same as that of working example 1.
[0034]When carried out on condition of above, the reaction time was able to disassemble the electroconductive glue 12 on which the quartz plate 10 and the ceramic package 11 are pasted up by 30min. Thereby, the quartz plates 10 and the ceramic packages 11 which are valuable inorganic substance part materials were able to be collected.
[0035]The functional characteristic of the quartz plate 10 collected in working example 3 and the ceramic package 11 was measured. The frequency of the quartz plate 10 was able to obtain a new part material and the characteristic by Table 1. The thickness and the insulation resistance value of the terminal 11a of the ceramic package 11 were also able to obtain a new part material and the characteristic.
[0036]The method of collecting and recycling a valuable inorganic substance part material for a short time was able to be provided by adding a small amount of additive agents to water, and performing a supercritical reaction according to working example 3.
[0037]
[Work example 4]Working example 4 performed the supercritical reaction using the water into which

the additive agent more than critical temperature and a pressure went the crystal oscillator 1. The operation condition performed the supercritical reaction by temperature;380 ** and pressure;24.3MPa. About mixing of the swelling agent, it was presupposed that it is the same as that of working example 1.

[0038]When carried out on condition of above, the reaction time was able to disassemble the electroconductive glue 12 on which the quartz plate 10 and the ceramic package 11 are pasted up by 60min. Thereby, the quartz plates 10 and the ceramic packages 11 which are valuable inorganic substance part materials were able to be collected.

[0039]The functional characteristic of the quartz plate 10 collected in working example 4 and the ceramic package 11 was measured. By Table 1, the frequency of the quartz plate 10 was able to obtain a new part material and the characteristic. The thickness and the insulation resistance value of the terminal 11a of the ceramic package 11 were also able to obtain a new part material and the characteristic.

[0040]The method of collecting and recycling a valuable inorganic substance part material was able to be provided by adding a small amount of additive agents to water, and performing a supercritical reaction according to working example 4.

[0041]

[Work example 5]As working example 5, the water more than critical temperature and a pressure performed the supercritical reaction for the crystal oscillator 1, without using a swelling agent. Relation condition performed the supercritical reaction by temperature;400 ** and pressure;28.9MPa.

[0042]When compared on condition of above, the reaction time was able to disassemble the electroconductive glue 12 on which the quartz plate 10 and the ceramic package 11 are pasted up by 60min. Thereby, the quartz plates 10 and the ceramic packages 11 which are valuable inorganic substance part materials were able to be collected. However, the reaction time of the more than performed in working example 1-3 is needed.

[0043]Next, the functional characteristic of the quartz plate 10 collected in working example 5 and the ceramic package 11 was measured. By Table 1, the frequency of the quartz plate 10 was a new part material and the characteristic. The thickness and the insulation resistance value of the terminal 11a of the ceramic package 11 were also a new part material and the characteristic.

[0044]

[Comparative example 1] After making the crystal oscillator 1 immersed in a swelling agent, the subcritical reaction was performed using the water below critical temperature and a pressure. Relation condition performed the subcritical reaction by temperature;280 ** and pressure;6.2MPa. About mixing of the swelling agent, it was presupposed that it is the same as that of working example 1.

[0045]When were compared on condition of above and the subcritical reaction was performed for 180 minutes, the electroconductive glue 12 on which the quartz plate 10 and the ceramic package 11 are pasted up was not able to be disassembled. Since the influence of a subcritical reaction was destroyed in pieces, the quartz plate 10 which is a valuable inorganic substance part material was not able to be estimated by it.

[0046]

[Table 1]

	温度 (℃)	圧力 (MPa)	膨潤剤	時間 (min.)	水晶板 発振数 (MHz)	セラミックパッケージ 端子隙間 (μm)	セラミックパッケージ 絶縁抵抗 (×10⁶Ω)
実施例1	400	28.9	あり	10	14.4	1.45	2.47
実施例2	380	24.3	あり	30	14.4	1.43	2.35
実施例3	400	28.9	あり	30	14.4	1.45	2.48
実施例4	380	24.3	あり	60	14.4	1.44	2.48
実施例5	400	28.9	なし	60	14.4	1.45	2.48
比較例1	280	6.2	あり	180	破壊	破壊	破壊
規格値	-	-	-	-	14.3-14.5	1.0-3.0	$<2.0\times10^{6}$

[0047]

[Effect of the Invention]By making the water which added the swelling agent and the oxidizer if needed immerse the electronic parts which were produced in malfunctioning according to the invention in this application, and using the supercritical water more than critical temperature and a pressure so that the above working example may also show. Either or combination of an additive, synergistic, or complementary operation can perform the oxidation reaction by swelling and supercritical water of a resinous principle, a resinous principle can be removed, and it can collect and reuse about a valuable inorganic substance part material, without being accompanied by change of a presentation, intensity, the fall of a function, etc.

[0048]The resinous principle which is the operation target of the invention in this application, The polymer alloys which which thermosetting or thermoplastic resin may be sufficient as, and consist of two or more kinds of ingredients, and those mixtures. Or the industrial effects, such as not needing large-scale neutralization equipment but becoming advantageous in cost, in order to be also able to make into an object further laminated material and the hardened material of the epoxy resin for which decomposition was conventionally difficult, or phenol resin and to use neither acid nor alkali in large quantities, are remarkable.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is an explanatory view of the crystal oscillator used for the recovery method of the inorganic substance part material from the electronic parts of this embodiment.
[Drawing 2]It is an explanatory view of the reaction apparatus used for the recovery method of the inorganic substance part material from the electronic parts of this embodiment.
[Description of Notations]
1 Crystal oscillator
10 Quartz plate
11 Ceramic package
11a Terminal
12 Electroconductive glue
2 Reaction apparatus
20 Coil
21 Wire
22 Sand bath
23 Operator control panel

[Translation done.]